

# Structure and Thermal Reactions of Dihydrogen Complexes: The IR Characterization of $M(\text{CO})_5(\text{H}_2)$ ( $M = \text{Cr}, \text{Mo},$ and $\text{W}$ ) and $\text{cis-Cr}(\text{CO})_4(\text{H}_2)_2$ in Liquid Xenon Solution and the Formation of HD during Exchange of $\text{H}_2$ and $\text{D}_2$

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**Abstract:** UV photolysis of  $M(\text{CO})_6$  ( $M = \text{Cr}, \text{Mo},$  and  $\text{W}$ ) and  $\text{H}_2$  in liquid Xe at  $-70^\circ\text{C}$  yields  $M(\text{CO})_5(\text{H}_2)$  and, for Cr and W,  $\text{cis-M}(\text{CO})_4(\text{H}_2)_2$ . For all three metals,  $M(\text{CO})_5(\text{H}_2)$  has been fully characterized from IR spectra, including  $^{13}\text{CO}$  data, C-O factored force field analysis, and observation of  $\nu(\text{H-H})$  bands. Surprisingly, the  $\nu(\text{H-H})$  band for Mo,  $3080\text{ cm}^{-1}$ , is at a higher wavenumber than Cr,  $3030\text{ cm}^{-1}$ , or W,  $2711\text{ cm}^{-1}$ . The thermal stability of the three compounds is in the order  $\text{Mo}(\text{CO})_5(\text{H}_2)$  (least stable)  $\ll$   $\text{Cr}(\text{CO})_5(\text{H}_2)$   $<$   $\text{W}(\text{CO})_5(\text{H}_2)$  (most stable). IR data for  $\text{Cr}(\text{CO})_5(\text{D}_2)$  and  $\text{Cr}(\text{CO})_5(\text{HD})$  are also presented. Similarly,  $\text{cis-Cr}(\text{CO})_4(\text{H}_2)_2$  has been characterized by  $^{13}\text{CO}$  enrichment.  $\text{Cr}(\text{CO})_5(\text{H}_2)$  undergoes an exchange reaction, at  $-70^\circ\text{C}$ , with  $\text{N}_2$  to form  $\text{Cr}(\text{CO})_5(\text{N}_2)$ , and  $\text{cis-Cr}(\text{CO})_4(\text{H}_2)_2$  forms exclusively  $\text{cis-Cr}(\text{CO})_4(\text{N}_2)_2$  under similar conditions via a detectable intermediate, probably  $\text{cis-Cr}(\text{CO})_4(\text{H}_2)(\text{N}_2)$ . Under a pressure of  $\text{D}_2$ ,  $\text{Cr}(\text{CO})_5(\text{H}_2)$  reacts thermally to form  $\text{Cr}(\text{CO})_5(\text{D}_2)$  but *not*  $\text{Cr}(\text{CO})_5(\text{HD})$ . However,  $\text{Cr}(\text{CO})_5(\text{HD})$  is formed during  $\text{H}_2/\text{D}_2$  exchange in  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$ . The HD is probably formed by intramolecular exchange in  $\text{Cr}(\text{CO})_4(\text{H}_2)(\text{D}_2) = \text{Cr}(\text{CO})_4(\text{HD})_2$ . By contrast, reaction of  $d^8$  metal centers with  $\text{H}_2$  in Xe solution does lead to formation of dihydrides. UV photolysis of  $\text{Ru}(\text{CO})_4\text{PPh}_3$  and  $\text{H}_2$  dissolved in supercritical Xe at room temperature yields  $\text{Ru}(\text{CO})_3(\text{H})_2\text{PPh}_3$ , an unstable dihydride, previously reported in thermal reactions at higher temperature.

Recent reports<sup>1-6</sup> of dihydrogen complexes of transition metals have aroused considerable interest. The first dihydrogen complexes to be isolated,  $M(\text{CO})_3(\text{PR}_3)_2(\text{H}_2)$  ( $M = \text{W}, \text{Mo}; \text{R} = i\text{-Pr}$  and  $\text{Cy}$ ) were fully characterized by Kubas and co-workers with use of X-ray and neutron diffraction and IR and NMR spectroscopy.<sup>1</sup> Together, these techniques established that coordination of dihydrogen by a  $d^6$  metal center does not necessarily require rupture of the H-H bond. This conclusion has been reinforced by a recent X-ray diffraction study<sup>6</sup> on a stable dihydrogen complex of Fe(II), another  $d^6$  center.

Although in Kubas's compound the phosphine substituents are necessary to impart thermal stability to the compounds, their presence does introduce complications into a theoretical analysis<sup>7</sup> of the bonding of  $\text{H}_2$ . Clearly, the unsubstituted carbonyl dihydrogen complexes,  $M(\text{CO})_5(\text{H}_2)$ , are rather simpler systems, both for theoretical<sup>8</sup> and spectroscopic studies.<sup>2,3</sup> Moreover, the chromium analogue,  $\text{Cr}(\text{CO})_5(\text{H}_2)$ , is of particular interest as it is a postulated intermediate in the water gas shift reaction.<sup>9</sup>

$\text{Cr}(\text{CO})_5(\text{H}_2)$  has been generated by UV photolysis of  $\text{Cr}(\text{CO})_6$  in the presence of  $\text{H}_2$  in hydrocarbon solution at room temperature,<sup>2,3</sup> in liquefied xenon solution<sup>2</sup> at  $\sim -70^\circ\text{C}$ , and in Ar matrices<sup>4</sup> at 20 K. However, it was only in liquid Xe that a sufficient concentration of  $\text{Cr}(\text{CO})_5(\text{H}_2)$  could be generated to detect the presence of coordinated dihydrogen. This was established by observation of an IR band at  $3030\text{ cm}^{-1}$ , characteristic of a  $\nu(\text{H-H})$  stretching vibration.<sup>2</sup> Liquefied Xe is a particularly good solvent for studying such complexes,<sup>10,11</sup> because it combines

complete transparency in the mid-IR with low temperatures which stabilize thermally unstable species. Most recently, we have used liquid Xe to generate two complexes,  $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$  and  $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$ , where dihydrogen is coordinated to metal centers with nominal  $d^{10}$  configurations.<sup>12</sup> This paper, however, is concerned with dihydrogen complexes of  $d^6$  metals and particularly with the thermal reactions of these compounds.

In what follows (i) we extend our preliminary studies<sup>2</sup> on  $\text{Cr}(\text{CO})_5(\text{H}_2)$  in liquid Xe to include the corresponding compounds of Mo and W; (ii) we characterize, in liquid Xe, the disubstituted complex  $\text{cis-Cr}(\text{CO})_4(\text{H}_2)_2$ , recently reported by Sweany in low-temperature matrices;<sup>4</sup> (iii) we examine the thermal reactions of these species with  $\text{N}_2$  and  $\text{D}_2$ , showing that  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$  plays a key role in the formation of HD; (iv) finally, we demonstrate that liquid Xe does not prevent the formation of metal dihydrides when the electronic configuration of the transition-metal center permits cleavage of the H-H bond.

## Experimental Section

The liquid-nitrogen-cooled cell for use with liquid xenon has been described in detail previously.<sup>10,11</sup> In the experiments here, we have made particular use of the relatively wide temperature range  $-111$  to  $-40^\circ\text{C}$  over which liquid Xe can be used in this cell. In a typical experiment,  $\text{H}_2$  or  $\text{D}_2$  was dissolved by pressurizing the cell with the appropriate gas after the cell had been filled with Xe and the metal carbonyl. Further details of the IR bands due to dissolved  $\text{H}_2$  and  $\text{D}_2$  are given elsewhere.<sup>12</sup>

Experiments in room temperature supercritical Xe were carried out in a commercial cell (Aminco Instrument Co. Model 41-11542) on loan from Professor V. Vaida. The cell was fitted with  $\text{CaF}_2$  windows of 28-mm diameter and 18 mm thick. It was filled with Xe at  $-10^\circ\text{C}$ , pressurized to 100 atm with  $\text{H}_2$ , and allowed to warm to room temperature. The critical temperature of Xe is  $+16^\circ\text{C}$  and the critical pressure 58 atm. **Safety Warning:** Such experiments involve high gas pressures and should be approached with due caution.

All IR spectra were recorded on a Nicolet MX-3600 interferometer with a Nicolet 1280 data system. Interferograms were usually collected

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**Table I.** Wavenumbers ( $\text{cm}^{-1}$ ) of Observed  $\nu(\text{C-O})$  Bands and C-O Factored Force Constants<sup>15</sup> ( $\text{N m}^{-1}$ ) for  $\text{M}(\text{CO})_5(\text{H}_2)$  Species in Liquid Xe at  $-70^\circ\text{C}$ 

A. Wavenumbers of Observed $\nu(\text{C-O})$ Bands						
Cr		Mo		W		assign <sup>b</sup>
obsd	$\Delta\nu^a$	obsd	$\Delta\nu^a$	obsd	$\Delta\nu^a$	
2094.0	0.2	2097.7	0	2098.2	0	0
2086.1	-0.1	2090.1 <sup>c</sup>	0.1	2090.3 <sup>c</sup>	-0.4	1 <sub>eq</sub>
2002.6	0	2004.6 <sup>c</sup>	0	1997.5 <sup>c</sup>	0	1 <sub>eq</sub>
1974.3	0	1978.7	-0.9	1972.2	0.1	0, 1 <sub>ax</sub> , 1 <sub>eq</sub> , (e mode) <sup>e</sup>
1971.9 sh	0.2	1971.5	0.1	(1971.4) <sup>d</sup>	0	0 (a <sub>1</sub> mode)
1948.4	-0.1	1947.2 <sup>c</sup>	-0.1	1940.8 <sup>c</sup>	-0.1	1 <sub>eq</sub>
1930.9	-0.5	1931.0 <sup>c</sup>	0	1932.5 <sup>c</sup>	0	1 <sub>ax</sub>

B. C-O Factored Force Constants			
	Cr	Mo	W
$k_{ax}$	1593.63	1592.67	1601.74
$k_{eq}$	1631.87	1637.86	1627.71
$k_{ax,eq}$	32.28	32.41	37.42
$k_{eq,eq\ cis}$	29.34	30.34	31.27
$k_{eq,eq\ trans}$	57.30	56.39	56.54

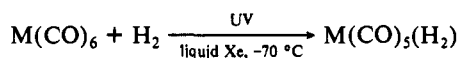
<sup>a</sup> Observed minus calculated wavenumbers ( $\text{cm}^{-1}$ ) using force constants listed below. <sup>b</sup> Molecules abbreviated as follows, 0,  $\text{M}(\text{CO})_5$ ; 1<sub>eq</sub>,  $\text{M}(\text{CO})_4(\text{CO}_{\text{equatorial}})$ ; 1<sub>ax</sub>,  $\text{M}(\text{CO})_4(\text{CO}_{\text{axial}})$ . <sup>c</sup> Measured from natural abundance  $^{13}\text{C}$ . <sup>d</sup> Obscured by e band, calculated value. <sup>e</sup> e mode for 0 and 1<sub>ax</sub>, a'' for 1<sub>eq</sub>.

with 16K data points ( $2\text{-cm}^{-1}$  resolution) or 32K data points ( $0.7\text{-cm}^{-1}$  resolution).  $\text{Cr}(\text{CO})_6$ ,  $\text{Mo}(\text{CO})_6$ , and  $\text{W}(\text{CO})_6$  (BDH Chemicals Ltd.),  $\text{H}_2$  and Xe (BOC Research Grade),  $\text{D}_2$  (99%, BDH), and HD (Amersham International) were all used without further purification.  $\text{Ru}(\text{CO})_4\text{PPh}_3$  were prepared by literature methods<sup>13</sup> and  $\text{Cr}(\text{CO})_5(^{13}\text{CO})$ <sup>14</sup> was a gift from Dr. F.-W. Grevels.

A 250-W high-pressure Hg arc ( $\lambda > 280\text{ nm}$ ) focused through quartz lenses was used for photolysis. The design of our cell<sup>11</sup> means that negligible stray UV light falls on the solution unless the photolysis lamp is switched on.

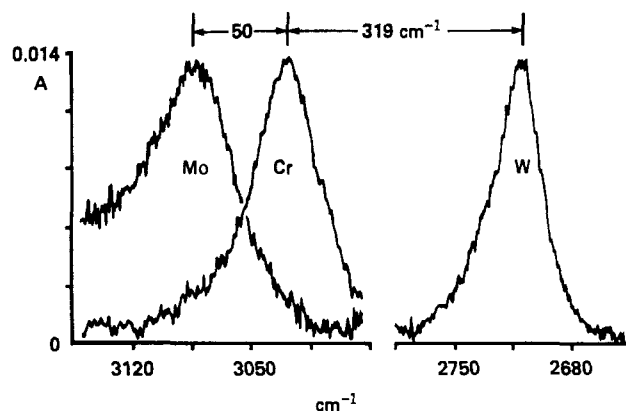
## Results

**$\text{Cr}(\text{CO})_5(\text{H}_2)$ ,  $\text{Mo}(\text{CO})_5(\text{H}_2)$ , and  $\text{W}(\text{CO})_5(\text{H}_2)$ .** We have generated  $\text{Mo}(\text{CO})_5(\text{H}_2)$  and  $\text{W}(\text{CO})_5(\text{H}_2)$  in liquid Xe by a route identical with that already used<sup>2</sup> to generate  $\text{Cr}(\text{CO})_5(\text{H}_2)$ .

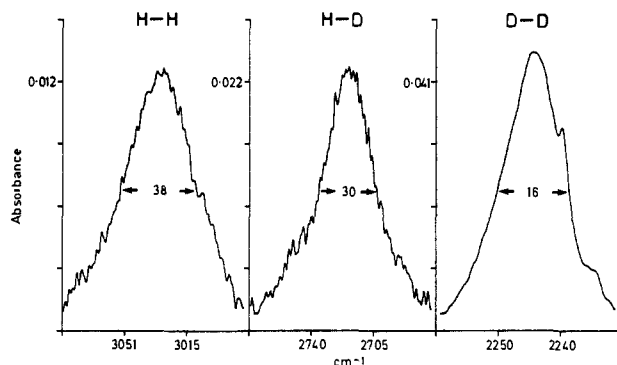


It can be seen from Table I that the  $\nu(\text{C-O})$  frequencies of all three compounds are similar. There are small differences between the metals, in particular, in the position of the low-frequency  $a_1$  band. This band appears as a shoulder on the side of the more intense e band of  $\text{Cr}(\text{CO})_5(\text{H}_2)$ ; it is totally obscured by the e band in  $\text{W}(\text{CO})_5(\text{H}_2)$  and is almost completely resolved from the e band of  $\text{Mo}(\text{CO})_5(\text{H}_2)$ . For each compound, we have used the additional information provided by the  $\nu(\text{C-O})$  bands of  $\text{M}(\text{CO})_4(^{13}\text{CO})(\text{H}_2)$  to show that the observed wavenumbers are consistent with the presence of a  $\text{C}_{4v}\text{M}(\text{CO})_5$  moiety. The C-O factored force constants,<sup>2,15</sup> listed in Table I, are remarkably similar for the three metals.

$\text{Cr}(\text{CO})_5(\text{H}_2)$  has an IR band at  $3030\text{ cm}^{-1}$  associated with the  $\nu(\text{H-H})$  vibration of the coordinated dihydrogen.<sup>2</sup> This band is illustrated in Figure 1, together with the corresponding IR bands of  $\text{Mo}(\text{CO})_5(\text{H}_2)$  and  $\text{W}(\text{CO})_5(\text{H}_2)$ . The absorption for the Mo compound is  $50\text{ cm}^{-1}$  higher than for Cr, while that for W is  $319\text{ cm}^{-1}$  lower. This difference between the three metals is striking, particularly in view of the similarities in the  $\nu(\text{C-O})$  region. Unfortunately, we were unable to observe  $\nu(\text{D-D})$  bands of either  $\text{Mo}(\text{CO})_5(\text{D}_2)$  or  $\text{W}(\text{CO})_5(\text{D}_2)$ , perhaps because they were ob-



**Figure 1.** IR spectra showing the substantial wavenumber shift between bands assigned to the  $\nu(\text{H-H})$  vibration of coordinated molecular dihydrogen in  $\text{Mo}(\text{CO})_5(\text{H}_2)$ ,  $\text{Cr}(\text{CO})_5(\text{H}_2)$ , and  $\text{W}(\text{CO})_5(\text{H}_2)$  in liquid Xe at  $-70^\circ\text{C}$ . Note that the three traces were recorded in separate experiments and that the absorbance scale refers to the Mo traces.



**Figure 2.** IR bands assigned to coordinated  $\text{H}_2$ , HD, and  $\text{D}_2$  in  $\text{Cr}(\text{CO})_5(\text{H}_2)$ ,  $\text{Cr}(\text{CO})_5(\text{HD})$ , and  $\text{Cr}(\text{CO})_5(\text{D}_2)$ , in liquid Xe at  $-70^\circ\text{C}$ . Note that the three bands are observed in separate experiments and are plotted with different absorbance and wavenumber scales. The arrows indicate the relative half-widths of the bands.

scured by other stronger absorptions (e.g.,  $\nu(\text{C-O})$  fundamentals, etc.).

It is interesting that the  $\nu(\text{H-H})$  band of  $\text{W}(\text{CO})_5(\text{H}_2)$  in liquid Xe,  $2711\text{ cm}^{-1}$ , is only  $21\text{ cm}^{-1}$  higher than the reported IR band of  $\text{W}(\text{CO})_3(\text{PCy}_3)_2(\text{H}_2)$ ,  $2690\text{ cm}^{-1}$ , in a Nujol mull at room temperature. One is tempted to speculate that the  $\nu(\text{H-H})$  frequency may be more influenced by the particular metal to which  $\text{H}_2$  is coordinated than by the other ligands attached to the metal.

$\text{Mo}(\text{CO})_5(\text{H}_2)$  appears to have a significantly lower thermal stability than the Cr and W compounds. At  $-74^\circ\text{C}$ ,  $\text{Mo}(\text{CO})_5(\text{H}_2)$  decayed with a half-life of 12 min, even under 10 atm of  $\text{H}_2$ . Under these conditions, both  $\text{Cr}(\text{CO})_5(\text{H}_2)$  and  $\text{W}(\text{CO})_5(\text{H}_2)$  did not decay appreciably over a period of several hours.  $\text{W}(\text{CO})_5(\text{H}_2)$  appears to be thermally the most stable of the three compounds. Compounds of Mo are often thermally less stable than their Cr and W analogues and the instability of  $\text{Mo}(\text{CO})_5(\text{H}_2)$  appears, in retrospect, quite consistent with the chemistry of many other compounds of the Group 6 metals. However, it is worth noting that stable  $\text{M}(\text{CO})_5(\text{PR}_3)_2(\text{H}_2)$  complexes are known for both Mo and W but the Cr analogue is still unknown.

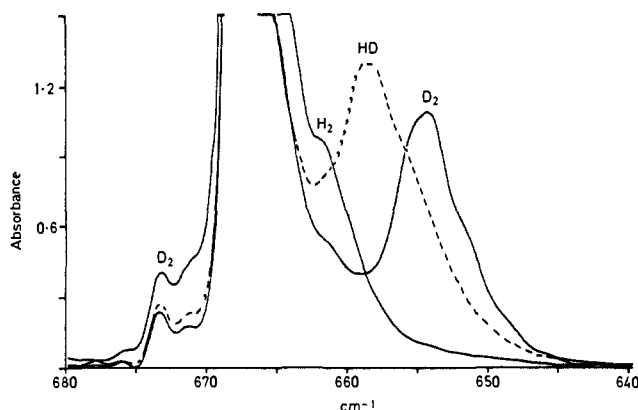
**$\text{Cr}(\text{CO})_5(\text{HD})$ .** We have already reported<sup>2</sup> the preparation of  $\text{Cr}(\text{CO})_5(\text{H}_2)$  and  $\text{Cr}(\text{CO})_5(\text{D}_2)$ . We have now prepared isotopically pure  $\text{Cr}(\text{CO})_5(\text{HD})$  in liquid Xe, by photolysis of  $\text{Cr}(\text{CO})_6$  in the presence of HD.  $\text{Cr}(\text{CO})_5(\text{HD})$  has a  $\nu(\text{H-D})$  band at  $2725\text{ cm}^{-1}$  compared to  $\nu(\text{H-H})$  of  $\text{Cr}(\text{CO})_5(\text{H}_2)$ ,  $3030\text{ cm}^{-1}$ , and  $\nu(\text{D-D})$  of  $\text{Cr}(\text{CO})_5(\text{D}_2)$ ,  $2242\text{ cm}^{-1}$ . The bands are illustrated in Figure 2. Although the isotopic shifts are all somewhat less than expected for the isolated diatomics,  $\text{H}_2$ , HD, and  $\text{D}_2$ , the position of the HD band, roughly midway between the  $\text{H}_2$  and  $\text{D}_2$  band, is very strong evidence for coordination of molecular dihydrogen without rupture of the H-D bond.

The spectra in Figure 2 do not provide sufficient information

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(14) Grevels, F.-W.; Skibbe, V. *J. Chem. Soc., Chem. Commun.* **1984**, 681.

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**Figure 3.** IR spectra showing low-frequency bands assigned to Cr(CO)<sub>5</sub>(H<sub>2</sub>), Cr(CO)<sub>5</sub>(HD), and Cr(CO)<sub>5</sub>(D<sub>2</sub>) in liquid Xe at -70 °C. As before, the three traces were recorded in separate experiments. The most intense absorption, which is not labeled, is due to unreacted Cr(CO)<sub>6</sub>.

**Table II.** Wavenumbers (cm<sup>-1</sup>) of Strongest IR Bands of Cr(CO)<sub>5</sub>(H<sub>2</sub>), Cr(CO)<sub>5</sub>(HD), and Cr(CO)<sub>5</sub>(D<sub>2</sub>) in Liquid Xe at -70 °C

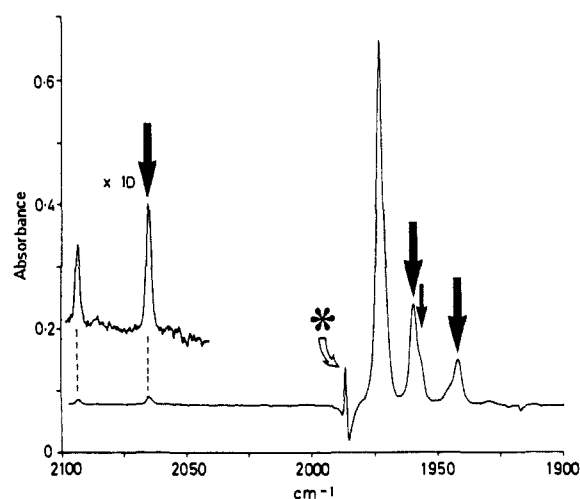
H <sub>2</sub>	HD	D <sub>2</sub>	assign <sup>t</sup>
3030			ν(H-H)
	2725		ν(H-D)
		2242	ν(D-D)
2093.9	2094	2093.8	ν(C-O) <sub>a1</sub>
1974.3	1974.8	1974.8	ν(C-O) <sub>e</sub>
1971.9	1971.6	1970.9	ν(C-O) <sub>a1</sub>
1379			ν(Cr-H <sub>2</sub> )?
661.2	659.4	654.6	?

to distinguish between sideways,  $\overline{M(H-H)}$  or end-on,  $M-H-H$  bonding of dihydrogen. It is, however, striking that the bands are broad. This broadness may be due to almost-free rotation of sideways-bonded dihydrogen. On the simplest level, one would expect that the bands of rotating molecules would have half-widths inversely related by the moments of inertia of H<sub>2</sub>, HD, and D<sub>2</sub> (i.e., in the ratio 1:0.75:0.5). This is quite close to the observed ratio (1:0.78:0.42), particularly in view of the difficulties in measuring the half-widths of such weak absorptions. A more rigorous analysis would need to allow for the center of rotation of coordinated H-D not coinciding with the center of mass,<sup>16</sup> but, unfortunately, our present data are insufficient for such a detailed analysis.

**Lower Frequency Vibrations of M(CO)<sub>5</sub>(H<sub>2</sub>).** We observed several very weak IR bands of Cr(CO)<sub>5</sub>(H<sub>2</sub>) and Cr(CO)<sub>5</sub>(D<sub>2</sub>) in the region, 1400–700 cm<sup>-1</sup>. Apart from a band at 1379 cm<sup>-1</sup> in the spectrum of Cr(CO)<sub>5</sub>(H<sub>2</sub>), there were no absorptions that could be unambiguously assigned to vibrations of the M-H<sub>2</sub> or M-D<sub>2</sub> units rather than overtone or combination bands. The band at 1379 cm<sup>-1</sup> may be due to the antisymmetric M-H<sub>2</sub> vibration, particularly because it is very close in frequency to the corresponding band<sup>12</sup> of Fe(CO)(NO)<sub>2</sub>(H<sub>2</sub>) at 1374 cm<sup>-1</sup>. However, the band of Cr(CO)<sub>5</sub>(H<sub>2</sub>) is very weak, and its assignment must be regarded as tentative. In the case of W(CO)<sub>5</sub>(H<sub>2</sub>), we did observe a stronger IR band at 919 cm<sup>-1</sup> that shifted to 678 cm<sup>-1</sup> in W(CO)<sub>5</sub>(D<sub>2</sub>). The ratio of wavenumbers of these two bands is identical with that reported by Kubas<sup>1</sup> for bands assigned to the symmetric W-H<sub>2</sub> (953 cm<sup>-1</sup>) and W-D<sub>2</sub> (703 cm<sup>-1</sup>) vibrations in W(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>).

For Cr(CO)<sub>5</sub>(H<sub>2</sub>), we found that IR bands in the region 680–650 cm<sup>-1</sup> showed small but reproducible shifts between H<sub>2</sub>, HD, and D<sub>2</sub> derivatives; see Figure 3. These shifts are similar to those reported<sup>4</sup> for matrix-isolated Cr(CO)<sub>5</sub>(H<sub>2</sub>). Although the precise origins of the shifts are not clear,<sup>17</sup> this region of the

(16) A similar problem arises with the rotation of matrix-isolated HD in an Ar cage. (Chanderasekharan, V., Fifth International Conference on Matrix Isolation, Fontevraud, 1985.)



**Figure 4.** IR spectrum in the ν(C-O) region, obtained after photolysis of Cr(CO)<sub>6</sub> and H<sub>2</sub> in liquid Xe at -111 °C. The arrowed bands are assigned to *cis*-Cr(CO)<sub>4</sub>(H<sub>2</sub>)<sub>2</sub> and the unlabeled bands are due to Cr(CO)<sub>5</sub>(H<sub>2</sub>). The asterisk marks the residual feature, left after computer subtraction of the IR band of unphotolyzed Cr(CO)<sub>6</sub>.

**Table III.** Observed and Calculated Wavenumbers for ν(C-O) Bands of *cis*-Cr(CO)<sub>4</sub>(H<sub>2</sub>)<sub>2</sub> and Its <sup>13</sup>CO Isotopomers in Liquid Xe Solution at -70 °C

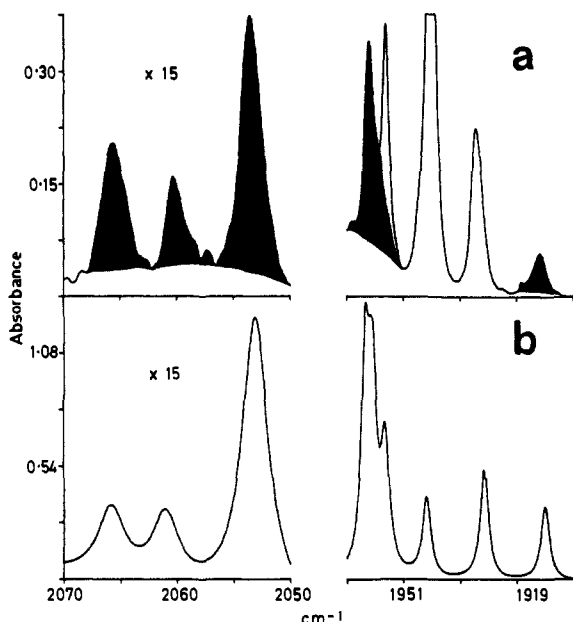
	obsd	calcd <sup>a</sup>
Cr( <sup>12</sup> CO) <sub>4</sub> (H <sub>2</sub> ) <sub>2</sub>	2065.9 (0.06) <sup>b</sup>	2065.8
C <sub>2v</sub>	1961.1 (1.0)	1961.8
	1958.9 <sup>c</sup> (0.83)	1959.8
	1943.7 <sup>d</sup> (0.37)	1944.6
Cr( <sup>12</sup> CO) <sub>3</sub> ( <sup>13</sup> CO)(H <sub>2</sub> ) <sub>2</sub>	2060.9	2061.0
<sup>13</sup> CO trans to H <sub>2</sub>	1958.9	1959.8
C <sub>s</sub>	<i>e</i>	1956.2
	1912.4	1911.1
Cr( <sup>12</sup> CO) <sub>3</sub> ( <sup>13</sup> CO)(H <sub>2</sub> ) <sub>2</sub>	2053.6	2053.1
<sup>13</sup> CO cis to H <sub>2</sub>	<i>e</i>	1961.4
C <sub>s</sub>	<i>e</i>	1944.6
	1930.7 <sup>d</sup>	1928.4
<i>cis</i> -W(CO) <sub>4</sub> (H <sub>2</sub> ) <sub>2</sub>	2078.5	
	1940.9	

<sup>a</sup> Calculated for a C<sub>2v</sub> Cr(CO)<sub>4</sub> geometry. Force constants (N m<sup>-1</sup>) k<sub>ax</sub> = 1614.1, k<sub>eq</sub> = 1564.9, k<sub>ax,eq</sub> = 37.99, k<sub>eq,eq,cis</sub> = 37.3, k<sub>eq,eq,trans</sub> = 62.5. Band intensities in Figure 5 were calculated by assuming an axial-axial bond angle of 141.7°, an axial-equatorial bond angle of 63.5°, and a dipole derivative of 0.83. <sup>b</sup> Figures in parentheses are the observed relative intensities. <sup>c</sup> This band shows a small shift to lower wavenumber ~0.8 cm<sup>-1</sup> when D<sub>2</sub> is used. <sup>d</sup> Position uncertain because of overlap with absorption of Cr(<sup>12</sup>CO)<sub>4</sub>(<sup>13</sup>CO)(H<sub>2</sub>)<sub>2</sub>; see Table I. <sup>e</sup> Obscured by other bands.

IR spectrum has been important in our present work for monitoring H/D exchange reactions (see below). The wavenumbers of the principal IR bands of Cr(CO)<sub>5</sub>(H<sub>2</sub>) and its HD and D<sub>2</sub> analogues are summarized in Table II.

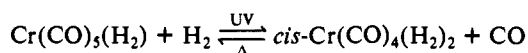
**Evidence for the Formation of *cis*-M(CO)<sub>4</sub>(H<sub>2</sub>)<sub>2</sub>, M = Cr and W.** Prolonged UV photolysis of Cr(CO)<sub>6</sub> and H<sub>2</sub> in liquid Xe leads to formation of a secondary photolysis product.<sup>10</sup> This

(17) Sweeney<sup>4</sup> tentatively assigned the 679-cm<sup>-1</sup> band of matrix-isolated Cr(CO)<sub>5</sub>(D<sub>2</sub>) to the symmetric ν(M-D<sub>2</sub>) stretching vibration. Since the absorption was poorly resolved in our experiments (see Figure 3) and since we did not see a corresponding band for Cr(CO)<sub>5</sub>(H<sub>2</sub>) at ~900 cm<sup>-1</sup>, we cannot confirm this assignment. A Reviewer has suggested that an alternative description of these vibrations would be a set of valence coordinates that reflect the dihydrogen as being an entity coordinated to the metal. This entity possesses one internal coordinate, the H-H stretch. The other coordinates would be defined by the motion of the H<sub>2</sub> molecule relative to the metal center. The symmetric and antisymmetric vibrations in Kubas's assignment<sup>1</sup> would then become respectively the motion representing the H<sub>2</sub> moiety moving back and forth along the M-H<sub>2</sub> bond axis and the H<sub>2</sub> rocking on the coordination sites.



**Figure 5.** (a) Observed  $\nu(\text{C-O})$  IR spectra of  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$  and  $\text{Cr}(\text{CO})_5(^{13}\text{CO})(\text{H}_2)_2$ , obtained by photolysis of  $\text{Cr}(\text{CO})_5(^{13}\text{CO})$  and  $\text{H}_2$  in liquid Xe at  $-70^\circ\text{C}$ . Uncolored bands are primarily due to unreacted  $\text{Cr}(\text{CO})_5(^{13}\text{CO})$  and  $\text{Cr}(\text{CO})_4(^{13}\text{CO})(\text{H}_2)_2$ . (b) Spectrum calculated for a *cis*- $\text{Cr}(\text{CO})_4$  moiety by using the force constants listed in Table III and a Lorentzian line shape,  $2.8\text{ cm}^{-1}$  FWHM.

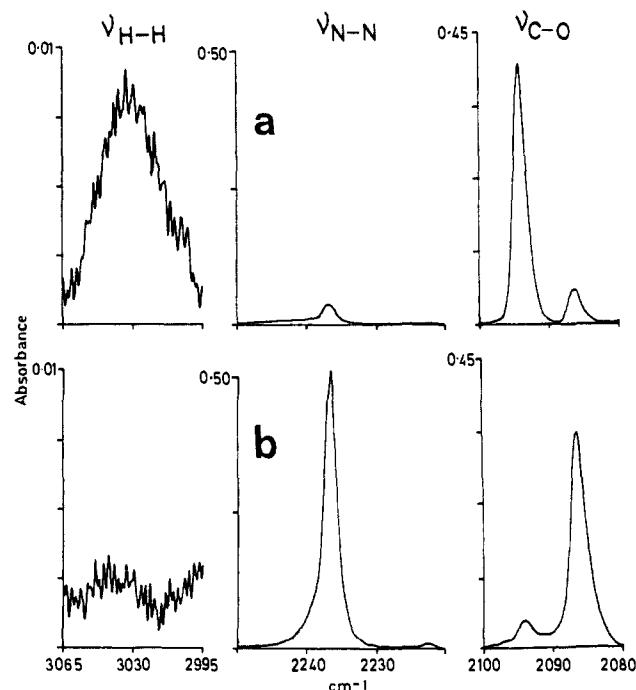
product is thermally rather less stable than  $\text{Cr}(\text{CO})_5(\text{H}_2)$  and relative yields are higher when the photolysis is carried out at lower temperatures. Figure 4 shows the IR spectrum obtained after UV photolysis at  $-111^\circ\text{C}$ , just above the freezing point of Xe under these conditions. The secondary photoproduct has four  $\nu(\text{C-O})$  IR bands, arrowed in Figure 4, but two of these bands overlap considerably. The wavenumbers of the bands are close to those assigned by Sweany to matrix-isolated *cis*- $\text{Cr}(\text{CO})_4(\text{H}_2)_2$ .<sup>18</sup> Changes in the intensities of IR bands show that the thermal decay of the photoproduct involves recombination with CO and regeneration of  $\text{Cr}(\text{CO})_5(\text{H}_2)$ . The decay approximately follows second-order kinetics.<sup>19</sup> Our observations suggest the following process:



By UV photolysis of  $\text{Cr}(\text{CO})_5(^{13}\text{CO})$  we observed further IR bands due to  $^{13}\text{CO}$  isotopomers of the secondary photoproduct. These additional bands provided sufficient data to test whether the observed spectrum was consistent with a  $C_{2v}$   $\text{Cr}(\text{CO})_4$  moiety in the photoproduct. The results of C-O factored force field calculations are summarized in Table III and the observed and calculated IR spectra are compared in Figure 5. Although the quantitative agreement is less good than we obtained in the case of  $\text{M}(\text{CO})_5(\text{H}_2)$ , the qualitative agreement between observed and calculated spectra is good. The poorer numerical fit may be due, in part, to overlapping absorptions of  $^{13}\text{CO}$ -enriched  $\text{Cr}(\text{CO})_5(\text{H}_2)$  and  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$ , which led to uncertainties in the frequencies of some bands of  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$ . The  $\nu(\text{C-O})$  spectra are therefore consistent with *cis*- $\text{Cr}(\text{CO})_4(\text{H}_2)_2$ . Surprisingly, we detected no bands assignable to the *trans* isomer. The other possible formulations of this compound,  $\text{Cr}(\text{CO})_4(\text{H})_4$  and  $\text{Cr}(\text{CO})_4(\text{H}_2)(\text{H})_2$ ,

(18) Sweany<sup>4</sup> only resolved three  $\nu(\text{C-O})$  bands for  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$ , 2067.8, 1965, and  $1945.4\text{ cm}^{-1}$ . His C-O force constant calculations predicted a fourth  $\nu(\text{C-O})$  band at  $1971\text{ cm}^{-1}$ , a region obscured by absorptions of  $\text{Cr}(\text{CO})_5(\text{H}_2)$ . Our spectra also have bands of  $\text{Cr}(\text{CO})_5(\text{H}_2)$  in the region of  $1971\text{ cm}^{-1}$ . However, computer subtraction of these bands from the spectra have failed to reveal any band of significant intensity attributable to  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$  in this region.

(19) At  $-70^\circ\text{C}$  and  $\sim 10\text{ atm}$  pressure of  $\text{H}_2$ , the intensities of the  $\nu(\text{C-O})$  bands of  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$  decrease with second-order kinetics (i.e.,  $1/\text{absorbance} = -kt$ , for a fivefold decrease in absorbance over 140 min).



**Figure 6.** IR spectra illustrating the thermal displacement of coordinated  $\text{H}_2$  from  $\text{Cr}(\text{CO})_5(\text{H}_2)$  by  $\text{N}_2$  in liquid Xe at  $-70^\circ\text{C}$ . (a)  $\nu(\text{H-H})$ ,  $\nu(\text{N-N})$ , and part of the  $\nu(\text{C-O})$  region of the spectrum, recorded immediately after the cell was pressurized with  $\text{N}_2$  (12 atm). (b) The spectrum 17 h later when the formation of  $\text{Cr}(\text{CO})_5(\text{N}_2)$  is almost complete. [Note that the lower frequency  $\nu(\text{C-O})$  band in (a) is partly due to  $\text{Cr}(\text{CO})_4(^{13}\text{CO})(\text{H}_2)_2$ ; see Table I.]

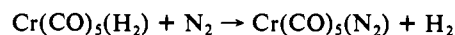
have respectively Cr(IV) and Cr(II) centers. These high oxidation states would be expected to shift the  $\nu(\text{C-O})$  bands to higher wavenumbers than observed.

Two  $\nu(\text{C-O})$  bands are observed on prolonged photolysis of  $\text{W}(\text{CO})_6$  and  $\text{H}_2$  in liquid Xe, and these may reasonably be assigned to *cis*- $\text{W}(\text{CO})_4(\text{H}_2)_2$ ; see Table III. Unfortunately, there was insufficient data to carry out a detailed  $^{13}\text{CO}$  analysis. No corresponding bands were observed during the photolysis of  $\text{Mo}(\text{CO})_6$ . Either  $\text{Mo}(\text{CO})_4(\text{H}_2)_2$  was not formed or it was too unstable to be observed under the conditions of our experiments.

Unfortunately, we have been unable to observe and IR bands that can be directly assigned to  $\nu(\text{H-H})$  or  $\nu(\text{D-D})$  vibrations of coordinated  $\text{H}_2$  or  $\text{D}_2$  in these  $\text{M}(\text{CO})_4(\text{H}_2)_2$  species. In all our experiments  $\text{M}(\text{CO})_5(\text{H}_2)$  was present in concentrations equal to or greater than  $\text{M}(\text{CO})_4(\text{H}_2)_2$ , and it may well be that the  $\nu(\text{H-H})$  bands of the two species overlap, particularly given the general broadness of the  $\nu(\text{H-H})$  absorptions.

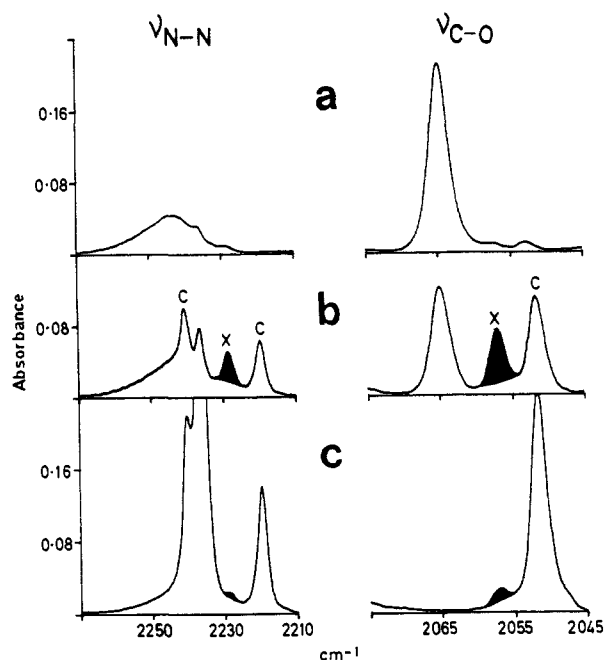
**Thermal-Exchange Reactions of  $\text{Cr}(\text{CO})_5(\text{H}_2)$  and  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$ .** The design of our high-pressure cell allows us to change the gases dissolved in the liquid Xe in less than 5 min. This is fast compared to the lifetimes of  $\text{Cr}(\text{CO})_5(\text{H}_2)$  and  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$  and so we have been able to study the thermal reactions of these compounds with  $\text{N}_2$  and with  $\text{D}_2$ .

**Thermal Reactions with  $\text{N}_2$ .**  $\text{Cr}(\text{CO})_5(\text{H}_2)$  reacts cleanly with  $\text{N}_2$  to give  $\text{Cr}(\text{CO})_5(\text{N}_2)$ , a compound that has previously been fully characterized<sup>20</sup> in liquid Xe. The reaction is relatively slow,  $t_{1/2} \sim 5\text{ h}$  at  $-60^\circ\text{C}$  under 12 atm of  $\text{N}_2$ , but conversion is nearly quantitative; see Figure 6.



The formation of  $\text{Cr}(\text{CO})_5(\text{N}_2)$  appears to be at least partially reversible. Under pressures of  $\text{H}_2$  and  $\text{D}_2$ ,  $\text{Cr}(\text{CO})_5(\text{N}_2)$  decays slowly to regenerate  $\text{Cr}(\text{CO})_5(\text{H}_2)$  or  $\text{Cr}(\text{CO})_5(\text{D}_2)$ . This observation is consistent with the report that, at room temperature,  $\text{Cr}(\text{CO})_5(\text{H}_2)$  and  $\text{Cr}(\text{CO})_5(\text{N}_2)$  have similar thermal stabilities.<sup>3</sup>

(20) See, e.g.: Turner, J. J.; Simpson, M. B.; Poliakov, M.; Maier, W. B., II; Graham, M. A. *Inorg. Chem.* 1983, 22, 911.



**Figure 7.** IR spectrum illustrating the two-stage displacement of D<sub>2</sub> from Cr(CO)<sub>4</sub>(D<sub>2</sub>)<sub>2</sub> by N<sub>2</sub> in liquid Xe at -70 °C. (a) The ν(N-N) and part of the ν(C-O) region before pressurizing the cell with N<sub>2</sub>. The unlabeled band in the ν(C-O) region is due to Cr(CO)<sub>4</sub>(D<sub>2</sub>)<sub>2</sub> and the broad band centered at ~2240 cm<sup>-1</sup> is due to coordinated D<sub>2</sub>; cf. Figure 2. (b) 30 min after pressurizing with N<sub>2</sub>. Bands colored black are due to the intermediate X, probably *cis*-Cr(CO)<sub>4</sub>(D<sub>2</sub>)(N<sub>2</sub>). Bands labeled C are due to *cis*-Cr(CO)<sub>4</sub>(N<sub>2</sub>)<sub>2</sub>. (c) 5.5 h after addition of N<sub>2</sub>. Note that X has largely decayed. The strong unlabeled band of ~2240 cm<sup>-1</sup> is due to Cr(CO)<sub>5</sub>(N<sub>2</sub>); cf. Figure 6.

Unfortunately, we cannot estimate a value of the equilibrium from our data.

The reaction of Cr(CO)<sub>4</sub>(H<sub>2</sub>)<sub>2</sub> with N<sub>2</sub> is rather more complex and interesting. The reaction proceeds in two stages.

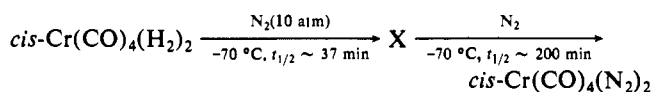
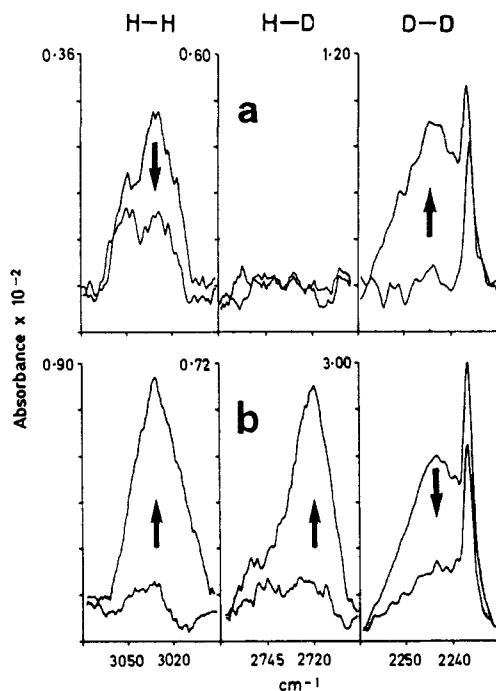


Figure 7 illustrates IR spectra for the reaction of Cr(CO)<sub>4</sub>(D<sub>2</sub>)<sub>2</sub>. The ν(N-N) region is particularly helpful for following the reaction because it immediately shows that (i) the intermediate product, X, must contain an N<sub>2</sub> ligand; (ii) the final product is the known compound<sup>20</sup> *cis*-Cr(CO)<sub>4</sub>(N<sub>2</sub>)<sub>2</sub>, bands marked C in Figure 7b. No *trans*-Cr(CO)<sub>4</sub>(N<sub>2</sub>)<sub>2</sub>, which has a ν(N-N) band<sup>20</sup> at 2170 cm<sup>-1</sup>, is formed. Thus, the *cis*-Cr(CO)<sub>4</sub> moiety is retained during substitution of H<sub>2</sub> by N<sub>2</sub>.

We have insufficient data to characterize the intermediate X fully, but it seems reasonable to suppose that it is *cis*-Cr(CO)<sub>4</sub>(H<sub>2</sub>)(N<sub>2</sub>). A calculation based on Timney's ligand effect constants,<sup>21</sup> predicts that the ν(N-N) band of *cis*-Cr(CO)<sub>4</sub>(H<sub>2</sub>)(N<sub>2</sub>) should occur at 2228 cm<sup>-1</sup>, precisely the position of the observed band of X. This agreement may well be fortuitous, but there are no other obvious structures for X.

UV photolysis of Cr(CO)<sub>5</sub>(N<sub>2</sub>) in liquid Xe yields both *cis* and *trans* isomers of Cr(CO)<sub>4</sub>(N<sub>2</sub>)<sub>2</sub>, presumably because the coordinatively unsaturated intermediate is fluxional.<sup>20</sup> It is particularly interesting, therefore, that the thermal reaction of *cis*-Cr(CO)<sub>4</sub>(H<sub>2</sub>)<sub>2</sub> yields only the *cis* isomer of Cr(CO)<sub>4</sub>(N<sub>2</sub>)<sub>2</sub>. This

(21) Timney's ligand effect constants (Timney, *J. Inorg. Chem.* **1979**, *18*, 2502) were originally devised for use with ν(C-O) vibrations. It has been shown, however, that they can also be applied successfully to ν(N-N) vibrations.<sup>20</sup> We have therefore calculated the appropriate ligand effect constants for dihydrogen from the C-O force constants of Cr(CO)<sub>5</sub>(H<sub>2</sub>),  $\epsilon_{\text{H}_2}^{90} = 18.3 \text{ N m}^{-1}$  and  $\epsilon_{\text{H}_2}^{180} = 72.6 \text{ N m}^{-1}$ . The other ligand effect constants required for calculating the frequencies ν(N-N) and ν(C-O) of *cis*-Cr(CO)<sub>4</sub>(H<sub>2</sub>)(N<sub>2</sub>) are available from ref 20 and Timney's original paper.

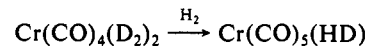


**Figure 8.** IR spectra illustrating H<sub>2</sub>/D<sub>2</sub> exchange in liquid Xe at -70 °C. (a) Displacement of H<sub>2</sub> from Cr(CO)<sub>5</sub>(H<sub>2</sub>) by D<sub>2</sub>. The two traces were recorded immediately after pressurizing the cell with D<sub>2</sub> and 3 h later. Note that no HD is formed during the reaction. (b) Displacement of D<sub>2</sub> from a mixture of Cr(CO)<sub>5</sub>(D<sub>2</sub>) and Cr(CO)<sub>4</sub>(D<sub>2</sub>)<sub>2</sub> by H<sub>2</sub>. Again, the first trace was recorded immediately after pressurizing the cell with H<sub>2</sub> and 1.5 h later. Note that in the presence of Cr(CO)<sub>4</sub>(D<sub>2</sub>)<sub>2</sub>, HD is formed. In both (a) and (b) the traces in the ν(H-H) and ν(H-D) regions have been digitally smoothed. The sharp band in the D-D region is due to trace quantities of Cr(CO)<sub>5</sub>(N<sub>2</sub>) present in the solution (cf. Figure 6).

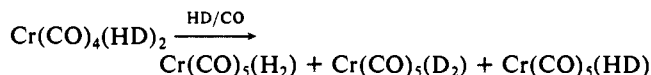
observation could perhaps be most easily explained if the reaction mechanism were associative in character. Similar associative processes may well be involved in hydrogenation reactions photocatalyzed by Cr(CO)<sub>6</sub>,<sup>22</sup> where a *cis*-Cr(CO)<sub>4</sub>(H<sub>2</sub>)(olefin) intermediate can be postulated.

**Thermal-Exchange Reactions with H<sub>2</sub> and D<sub>2</sub>.** Cr(CO)<sub>5</sub>(H<sub>2</sub>) reacts thermally with excess D<sub>2</sub> to generate Cr(CO)<sub>5</sub>(D<sub>2</sub>). No trace of Cr(CO)<sub>5</sub>(HD) can be detected, Figure 8a. There is no increase in IR absorption at 2725 cm<sup>-1</sup>, ν(H-D) of Cr(CO)<sub>5</sub>(HD). Similarly, there are no observable bands at ~660 cm<sup>-1</sup> due to Cr(CO)<sub>5</sub>(HD) (not illustrated). Such an exchange reaction without formation of HD is exactly what would be expected for compounds containing coordinated molecular dihydrogen and dideuterium. Qualitatively, H<sub>2</sub>/D<sub>2</sub> exchange occurs at a rate similar to H<sub>2</sub>/N<sub>2</sub> exchange (see above).

By contrast, HD is formed in thermal H<sub>2</sub>/D<sub>2</sub> exchange reactions of Cr(CO)<sub>4</sub>(H<sub>2</sub>)<sub>2</sub>. We observe this process indirectly by the growth of IR bands due to Cr(CO)<sub>5</sub>(HD). Figure 8b shows the results of an experiment where Cr(CO)<sub>5</sub>(D<sub>2</sub>) was reacted with H<sub>2</sub> in the presence of Cr(CO)<sub>4</sub>(D<sub>2</sub>)<sub>2</sub>. The ν(H-D) band of Cr(CO)<sub>5</sub>(HD) clearly grew during the reaction.



Similarly, we have shown that both Cr(CO)<sub>5</sub>(H<sub>2</sub>) and Cr(CO)<sub>5</sub>(D<sub>2</sub>) are formed when a mixture of Cr(CO)<sub>5</sub>(HD) and Cr(CO)<sub>4</sub>(HD)<sub>2</sub> is left standing under a pressure of HD.



(22) See, e.g.: Platbrood, G.; Wilputte-Steinert, L. *J. Organomet. Chem.* **1974**, *70*, 407. Wrighton, M. S.; Schroeder, M. A. *J. Am. Chem. Soc.* **1973**, *95*, 5764. Darendbourg, D. J.; Nelson, H. H., III; Murphy, M. A. *Ibid.* **1977**, *99*, 896.

**Table IV.** Wavenumbers (cm<sup>-1</sup>) of  $\nu(\text{C-O})$  and  $\nu(\text{Ru-H})$  Bands in Supercritical Xe at Room Temperature and in Heptane at 100 °C

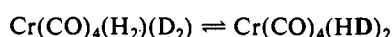
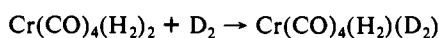
	supercritical Xe <sup>a</sup>	heptane <sup>b</sup>
Ru(CO) <sub>4</sub> PPh <sub>3</sub>	2063.5	2061
	(2038.2?)	
	1990.3	1987
	1958	1955
	1922	1919
Ru(CO) <sub>3</sub> (H) <sub>2</sub> PPh <sub>3</sub>	2090	2089 vw sh
	2082	2080 s
	2023.7	2021 vs
	2013.5	2010 sh
$\nu(\text{Ru-H})$	1892.3	1908 vw
	1810	

<sup>a</sup>This work; see Figure 9. <sup>b</sup>Reference 13, under 550 atm H<sub>2</sub>.

The formation of HD from H<sub>2</sub> and D<sub>2</sub> by heterogeneous catalysis is well-known at these temperatures.<sup>23</sup> Nevertheless, the formation of HD in liquid Xe appears to be a homogeneous reaction. Although several different metals (Cu, Fe, Pb, etc.) are used in the construction of our cell<sup>10,11</sup> and although prolonged UV photolysis of Cr(CO)<sub>6</sub> could possibly produce some finely divided Cr metal, there is no evidence that HD is formed by heterogeneous catalysis in our experiments.

The presence of Cr(CO)<sub>4</sub>(H<sub>2</sub>)<sub>2</sub> is essential for the formation of HD, but the mechanism is not completely clear. We are hampered by not observing any IR bands unambiguously associated with coordinated H<sub>2</sub> or D<sub>2</sub> in the disubstituted compound. The reaction does not appear to be catalytic in so far as the formation of Cr(CO)<sub>5</sub>(HD) is accompanied by the decay of Cr(CO)<sub>4</sub>(H<sub>2</sub>)<sub>2</sub>. UV photolysis of the solution immediately after the thermal-exchange reaction does not cause an increase in the intensity of the IR bands of Cr(CO)<sub>5</sub>(HD), suggesting that the solution does not contain appreciable amounts of uncoordinated HD. However, we have observed that prolonged UV photolysis of Cr(CO)<sub>6</sub> under pressures of H<sub>2</sub>/D<sub>2</sub> mixtures does promote formation of Cr(CO)<sub>5</sub>(HD), presumably via Cr(CO)<sub>4</sub>(H<sub>2</sub>)(D<sub>2</sub>).

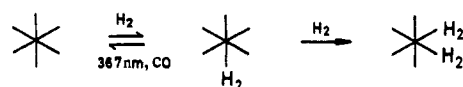
The most plausible mechanism therefore involves H<sub>2</sub>/D<sub>2</sub> exchange to yield Cr(CO)<sub>4</sub>(H<sub>2</sub>)(D<sub>2</sub>) followed by intramolecular formation of HD, a process reminiscent of olefin metathesis. Cr(CO)<sub>5</sub>(HD) can then easily be formed by reaction with free CO in the solution



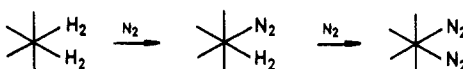
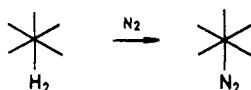
The intramolecular exchange reaction is somewhat akin to the reported fluxional processes in metal hydride-dihydrogen complexes, containing the H—M(H—H) moiety.<sup>5,6</sup> In these compounds, intramolecular exchange occurs between the terminal hydride and the hydrogens in the  $\eta^2\text{-H}_2$  ligand. It is not yet clear whether production of HD in Cr(CO)<sub>4</sub>(H<sub>2</sub>)(D<sub>2</sub>) involves a concerted process or the transient formation of a dihydride.<sup>24</sup> Nevertheless, our experiments do imply that the simultaneous coordination of two dihydrogen molecules to the same metal center greatly reduces the activation energy for intramolecular exchange.

**Formation of Dihydrides in Supercritical Xe.** (See Safety Warning in the Experimental Section). All of our experiments have been carried out in a somewhat exotic solvent, liquid Xe. It is important, therefore, to show that this solvent does not prevent the formation of metal dihydrides if the energetics are otherwise favorable. We have proven this by preparing the dihydride Ru(CO)<sub>3</sub>(H)<sub>2</sub>PPh<sub>3</sub>, a compound of catalytic interest that has pre-

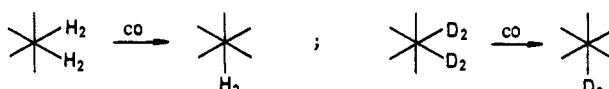
### Scheme I Photochemistry



### Thermal exchange with N<sub>2</sub>

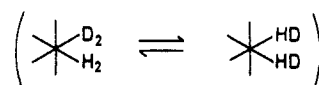
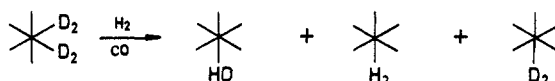
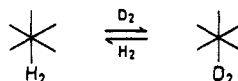


### Thermal reaction with CO



### Scheme II

#### Thermal exchange of H<sub>2</sub> and D<sub>2</sub>



viously been observed<sup>13</sup> in thermal reactions under high pressures of H<sub>2</sub>.



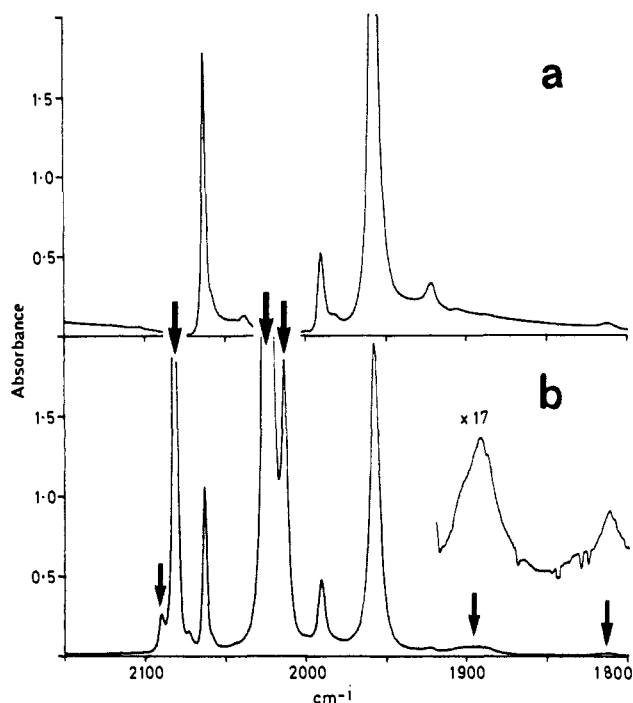
The precursor, Ru(CO)<sub>4</sub>PPh<sub>3</sub>, is only very sparingly soluble in liquid Xe at low temperature, but fortunately it is much more soluble in supercritical Xe at room temperature.<sup>25</sup> Ru(CO)<sub>3</sub>(H)<sub>2</sub>PPh<sub>3</sub> is produced in high yield by UV photolysis of Ru(CO)<sub>4</sub>PPh<sub>3</sub> under ~50 atm of H<sub>2</sub> in supercritical Xe; see Figure 9 and Table IV. The IR spectra are better than those obtained in hydrocarbon solvents.<sup>13</sup> We have, for example, observed a second  $\nu(\text{M-H})$  band ~1810 cm<sup>-1</sup> that has not previously been observed. The dihydride is thermally unstable under these conditions and slowly decays by second-order kinetics to unidentified products.

Thus, coordination of H<sub>2</sub> to a d<sup>8</sup> metal center leads to a dihydride in Xe solution, just as it does in other solvents. It is,

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(25) UV photolysis of W(CO)<sub>6</sub> and H<sub>2</sub> in supercritical Xe at room temperature leads to formation of the same dihydrogen compound, W(CO)<sub>5</sub>(H<sub>2</sub>), as observed at low temperature.



**Figure 9.** IR spectra showing the synthesis of  $\text{Ru}(\text{CO})_3(\text{H})_2\text{PPh}_3$  by photolysis of  $\text{Ru}(\text{CO})_4\text{PPh}_3$  and  $\text{H}_2$  in *supercritical* Xe at  $25^\circ\text{C}$ : (a) before photolysis; (b) after photolysis. Bands due to  $\text{Ru}(\text{CO})_3(\text{H})_2\text{PPh}_3$  are arrowed; note the lower wavenumber  $\nu(\text{Ru}-\text{H})$  region is also shown with an expanded absorbance scale.

therefore, most unlikely that our observations on  $d^6$  metal centers have been grossly influenced by the nature of the solvent. The chemistry of  $\text{Cr}(\text{CO})_5(\text{H}_2)$  and  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$  will almost certainly be similar in more conventional solvents.

### Conclusions

Schemes I and II summarize our observations on the photochemical and thermal reactions of  $\text{Cr}(\text{CO})_5(\text{H}_2)$  and  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$ . It must be stressed that all of the species in the schemes have been detected by IR spectroscopy in our experiments.  $\text{Cr}(\text{CO})_5(\text{H}_2)$  has now been exhaustively characterized, and the evidence for the structure of *cis*- $\text{Cr}(\text{CO})_4(\text{H}_2)_2$  is also strong. Perhaps the most interesting observations are (i) the specific

formation of *cis*- $\text{Cr}(\text{CO})_4(\text{N}_2)_2$  by reaction of *cis*- $\text{Cr}(\text{CO})_4(\text{H}_2)_2$  with  $\text{N}_2$  and (ii) the production of HD from  $\text{H}_2$  and  $\text{D}_2$  in the presence of *cis*- $\text{Cr}(\text{CO})_4(\text{H}_2)_2$ . It is probable that formation of HD involves intramolecular exchange in *cis*- $\text{Cr}(\text{CO})_4(\text{H}_2)(\text{D}_2)$ . This exchange would almost certainly be easier to monitor by NMR than IR. Preliminary NMR experiments in our laboratory on organometallic species in liquid Xe have been most encouraging<sup>26</sup> and we believe that a combination of IR and NMR techniques will eventually unravel the  $\text{H}_2/\text{D}_2$  exchange process.

Liquefied Xe provides general routes to whole groups of unstable organometallic compounds. It has already been used to characterize a wide range of dinitrogen complexes,<sup>10,20</sup> and here we have exploited its properties to study a range of compounds containing coordinated dihydrogen. Liquefied Xe does not pretend to be an appropriate solvent for large-scale syntheses. What it does provide is a quick route to small quantities of compounds under conditions where they can be examined spectroscopically and where their thermal stability can be established. In these circumstances, IR spectroscopy becomes a tool of unusual sensitivity, yielding a large amount of data about coordinated ligands.<sup>12,27</sup> Some of the species described in this paper are of considerable relevance to catalytic hydrogenation, and liquefied Xe has a very promising future in elucidating the mechanism of homogeneously catalyzed reactions.

**Acknowledgment.** We thank the Science and Engineering Research Council, ICI New Science Group and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for supporting this research. We are particularly grateful to Dr. G. E. Gadd and Dr. M. B. Simpson for their help with the initial experiments. We thank Professor J. K. Burdett, Professor D. D. Eley, J. G. Gamble, Dr. M. A. Healy, G. J. Miller, and Dr. R. Whyman for their help and advice. We are grateful to Professor V. Vaida for the loan of a high-pressure cell and to Dr. F.-W. Grevels for a gift of  $\text{Cr}(\text{CO})_5(^{13}\text{CO})$ .

**Registry No.**  $\text{Cr}(\text{CO})_5(\text{H}_2)$ , 102286-49-7;  $\text{Mo}(\text{CO})_5(\text{H}_2)$ , 102286-50-0;  $\text{W}(\text{CO})_5(\text{H}_2)$ , 102286-51-1;  $\text{Cr}(\text{CO})_6$ , 13007-92-6;  $\text{Mo}(\text{CO})_6$ , 13939-06-5;  $\text{W}(\text{CO})_6$ , 14040-11-0;  $\text{Cr}(\text{CO})_5(\text{HD})$ , 102286-52-2; *cis*- $\text{Cr}(\text{CO})_4(\text{H}_2)_2$ , 102286-53-3; *cis*- $\text{W}(\text{CO})_4(\text{H}_2)_2$ , 102286-54-4; *cis*- $\text{Cr}(\text{CO})_4(\text{N}_2)_2$ , 84130-32-5;  $\text{Cr}(\text{CO})_5(\text{N}_2)$ , 34416-63-2;  $\text{Cr}(\text{CO})_5(\text{D}_2)$ , 102286-55-5;  $\text{Cr}(\text{CO})_4(\text{HD})_2$ , 102286-56-6;  $\text{Cr}(\text{CO})_4(\text{H}_2)(\text{D}_2)$ , 102286-57-7;  $\text{Ru}(\text{CO})_3(\text{H})_2\text{PPh}_3$ , 42781-57-7;  $\text{H}_2$ , 1333-74-0;  $\text{Ru}(\text{CO})_4\text{PPh}_3$ , 21192-23-4.

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